

DERWENT-ACC-NO: 1994-243454

DERWENT-WEEK: 199430

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TITLE: Hologram recording material for mtr. of vol-
phase

hologram includes high molecular cpd. of vinyl
monomer, unsatd. complex
cpd. having at least one polymerisable ethylene
bond, cyanine dye and sulphonium organic boron

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PATENT-ASSIGNEE: TOYO INK MFG CO [TXW]

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PATENT-FAMILY:

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PUB-DATE June 24, 1994
LANGUAGE JA

APPLICATION-DATA:

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December 4, 1992

INT-CL-CURRENT:

TYPE IPC
DATE
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CIPS G03F7/027 20060101
CIPS G03F7/028 20060101
CIPS G03F7/029 20060101
CIPS G03F7/038 20060101
CIPS G03H1/02 20060101

ABSTRACTED-PUB-NO: JP 06175565 A

BASIC-ABSTRACT:

A hologram recording material includes the combination of (A) high
mol. cpd. of
the single polymer of vinyl monomer or copolymer of at least two

vinyl monomers, (B) the cpd. having at least one polymerisable ethylene unsaturated bond, (C) cyanine dye and (D) sulphonium organic boron complex. The cpd. (A) has the crosslinkable (meth)acryloyl gp. The difference of refractive index of the high mol. cpd. of (A) and that of the cpd. (B) is not less than 0.005.

The manufacturing of the hologram by using the hologram recording material comprises exposing the recording material, and then applying the light and/or heat to the same.

pref. the high mol. cpd. having crosslinkable (meth)acryloyl gp., is obtd. by introducing the vinyl monomer having a functional gp. such as hydroxyl gp., carboxyl gp., phosphoric gp., chloromethyl gp. or epoxy gp., to the polymer of the vinyl monomer.

USE/ADVANTAGE - The vol. phase-type hologram having high sensitivity throughout the wide wavelength area, and chemically stabilised, can be obtd. The hologram of high definition, high refractive index and high transparency can be easily mfd.

CHOSEN-DRAWING: Dwg.1/1

TITLE-TERMS: HOLOGRAM RECORD MATERIAL MANUFACTURE VOLUME PHASE HIGH MOLECULAR COMPOUND POLYVINYL MONOMER ONE POLYMERISE ETHYLENE UNSATURATED BOND CYANINE DYE SULPHONIUM ORGANIC BORON COMPLEX

DERIVENT-CLASS: A89 E19 G06 P84 V07

CPI-CODES: A08-C04; A08-C07; A11-C02B; A12-I02C; E05-C02; E10-A01; E25-B03;

G06-D; G06-E; G06-F03B; G06-F03C; G06-F03D; G06-G18;

EPI-CODES: V07-F02C;

CHEMICAL-CODES:

Chemical Indexing M3 *01*

Fragmentation Code

G016 C216 F012 F013 F014 F015 F016 F220 G010 G019
G020 G021 G029 G030 G031 G032 G039 G040 G050 G051
G100 G111 G112 G553 G563 G599 H721 H731 J581 K0
K422 K432 K433 K441 K442 L145 L199 L7
L730

M113 M115 M116 M119 M121 M122 M123 M124 M125 M126
M129 M142 M146 M147 M148 M210 M211 M212 M213 M214
M215 M216 M220 M221 M222 M223 M224 M225 M226 M231
M232 M233 M271 M272 M280 M281 M282 M283 M311 M312
M313 M314 M315 M316 M320 M321 M322 M323 M331 M332
M333 M334 M342 M343 M371 M373 M391 M392 M393 M413
M414 M415 M416 M510 M520 M521 M530 M531 M532 M540
M541 M542 M543 M772 M782 Q130 Q349 R043

Markush Compounds

9430B8503

Chemical Indexing M3 *02*

Fragmentation Code

B405 B505 B720 B744 B805 B831 G010 G020 G021 G040
G100 G111 G112 G113 H721 H731 M121 M122 M124 M129
M144 M210 M211 M212 M213 M214 M215 M216 M220 M221
M222 M223 M224 M225 M226 M231 M232 M233 M250 M280
M281 M282 M283 M311 M312 M313 M314 M315 M316 M320
M321 M322 M323 M331 M332 M333 M342 M351 M361 M391
M392 M393 M414 M416 M510 M520 M530 M531 M532 M533
M540 M620 M772 M782 Q130 Q349 R043

Markush Compounds

9430B8503

Chemical Indexing M4 *03*

Fragmentation Code

D012 D014 D016 D019 D601 D602 D621 D622 D711
D712 E160 E199 E250 E299 E400 E499 E520 E599 E600
E699 E810 E850 E860 E899 E910 E999 G001 G002 G010
G011 G012 G013 G019 G020 G021 G022 G029 G036 G038
G040 G100 G111 G112 G221 G299 G562 H1 H141 H142
H181 H182 H2 H201 H202 H7 H713 H716 H720 H721
H722 H723 H724 H725 H731 L721 M1 M126 M129 M132
M134 M139 M210 M211 M212 M213 M214 M215 M216 M220
M221 M222 M223 M224 M225 M226 M231 M232 M233 M240
M273 M280 M281 M282 M283 M311 M313 M315 M321 M322
M342 M412 M416 M512 M520 M530 M531 M532 M540 M541
M782 Q130 Q349 R043 W030 W335

Ring Index Numbers

02702 02933

Markush Compounds

9430B8801

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]
 017 ; G00260*R G0022 D01 D12 D10 D51 D53 ; G0022*R D01 D51 D53
 F26*R F35*R
 F54 F47 D60 D69 C1 7A D58 D22*R ; H0011*R ; H0011*R ; M9999
 M2073 ; L9999
 L2391 ; L9999 L2073 ; P0464*R D01 D22 D42 F47 ; K9847*R K9790 ;
 P0088 ;
 Polymer Index [1.2]
 017 ; ND01 ; Q9999 Q8640 Q8606 ; B9999 B4580 B4568 ; B9999 B4386
 B4240 ;
 B9999 B4444 B4240 ; B9999 B4397 B4240 ; N9999 N6177*R ;
 Polymer Index [1.3]
 017 ; D12 D10 D51*R ; A999 A179 A157 ;
 Polymer Index [1.4]
 017 ; D01 D61*R B* 3A S* 6A ; A999 A179 A157 ;

POLYMER-MULTIPUNCH-CODES-AND-KEY-SERIALS:
 Key Serials : 0004 0037 0069 0138 0141 0144 0165 0168 0171 0201 0207
 0209 0231
 1282 2016 2020 2194 2198 2301 2371 2413 2493 2594 2596 2607 2809
 Multipunch Codes: 038 04- 05- 06- 062 063 075 084 094 09- 104 15- 19-
 204 20-
 226 228 231 341 353 359 387 428 473 48- 516 522 524 541 545 546 634
 658

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 Non-CPI Secondary Accession Numbers: 1994-192076

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技術表示箇所					

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(22) 出願日	平成4年(1992)12月4日								

(54) 【発明の名称】 ホログラム記録材料及びそれを用いた体積位相型ホログラムの製造方法

(57) 【要約】
【目的】 優れた感度を示すホログラム記録材料及びそれを用いた体積位相型ホログラムの製造方法を提供することを目的とする。
【構成】 ビニルモノマーの単一重合体または2成分以上のビニルモノマーの共重合体である高分子化合物(A)、重合可能なエチレン性不飽和結合を少なくとも1個以上有する化合物(B)、シラン化合物(C)とスルホニウム有機ホウ素錯体(D)との組合せによりなるホログラム材料と、該ホログラム記録材料をホログラム露光の機、実および(または)熱を加える体積位相型ホログラムの製造方法。

【特許請求の範囲】

【請求項1】 エルミオノアの単一重合体または2成分以上のエルミオノアの共重合体である高分子化合物

(A)、重合可能なエチレン不飽和結合を有する高分子化合物を少なくとも

1個以上有する化合物(B)、シアニロ基を有する高分子化合物(C)及び

アルホニア有機ホウ素錯体(D)の組み合わせを含む

ことを特徴とするホロプラマ記録材料。

【請求項2】 エルミオノアの単一重合体または2成分以上のエルミオノアの共重合体である高分子化合物

(A)が、架橋可能なメタアクリロイドを有する

ことを特徴とする請求項1記載のホロプラマ記録材料。

【請求項3】 請求項1記載のホロプラマ記録材料。

【請求項4】 エルミオノアの単一重合体または2成分以上のエルミオノアの共重合体である高分子化合物

を有する化合物(B)、シアニロ基を有する化合物(C)及び

アルホニア有機ホウ素錯体(D)の組み合わせを含む

ことを特徴とする請求項1ないし3いれが記載のホロ

プラマ記録材料を用いてホロプラマを製造するにあつ

て、記録材料をホロプラマ露光したのち、光および

(または)熱を加えることを特徴とする体積位相型ホロ

プラマの製造方法。

【0001】

【産業上の利用分野】本発明は、化学的安定性及耐環境

特性に優れ、広い波長領域において高い感度特性を持

ち、且つ解読、回折効率及び透明性に優れたホロプラ

マ記録材料及びそれを用いて簡単に体積位相型ホロプラ

マの製造方法に関するものである。

【0002】

従来、ホロプラマ記録材料として、炭

白黒顔料および重クロム酸セラチン系の感光材料が一

般に使用されてきた。しかし、これを用いたホロプラ

マ材料は、ともに複雑な感光現像処理を必要とし、さら

に使用上における感度特性に劣る、あるいはホロプラマの

長期保存における感度特性に劣る、あるいはホロプラマの

長期保存における感度特性に劣る、あるいはホロプラマの

製造において感光現像工程を採用していないなどの製造上

の煩雑性、また、溶液浸漬操作時に生じる空層やひび割

れに起因する現像ムラや、白化による透明性の低下と

の問題が生じるなどの欠点を有していた。また、使用さ

れる重合体が非弾性であるために、硬化膜の強度に劣

るという欠点があった。

【0004】一方、ホロプラマの製造工程において複雑

な工程は煩雑な感光現像工程を必要としない、唯一の

と可能なフトリバーを使ったホロプラマ記録材料

(および)あるいはその製造方法が知られている。例え

ば、特開平2-3081号公報あるいは特開平2-303

82号公報においては、ポリマーあるいはモノマーの

うちから一方が芳香族あるいはイソプレンを含有する置換基

を有することを特徴とする置換基がポリマーと液体ニチ

ンゲンモノマー、及び光開始剤から構成されるホロプラ

マ記録用光重合性基剤混合物及び屈折率異質用エレクトロ

ンゲンモノマー、及び光開始剤から構成されるホロプラ

マ記録材料の長波長領域における感度特性は、数1

00 mJ/cm²オーダーであり、ホロプラマの強度に

劣る感度特性を有する化合物の組み合わせにより一層向上

させることが望まれた。

【0005】また、特開平2-51188号公報においては、

炭素二重結合を有する化合物の組み合わせにより、屈折率

に劣る感度特性を有する化合物の組み合わせにより、屈折率

に劣る感度特性を有する化合物の組み合わせにより、屈折率

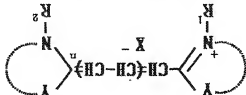
に劣る感度特性を有する化合物の組み合わせにより、屈折率

に劣る感度特性を有する化合物の組み合わせにより、屈折率

に劣る感度特性を有する化合物の組み合わせにより、屈折率

に劣る感度特性を有する化合物の組み合わせにより、屈折率

に劣る感度特性を有する化合物の組み合わせにより、屈折率

[illegible](1) ~~201~~—[9100]

(1) 100

【0015】本発明で使用するシアニン色素(C)は、一物などが挙げられる。

7. 2015年1月1日現在、本邦に在籍する外国人の人口は、約1,200万人と推定される。このうち、約1,000万人が労働力として本邦に在籍している。このうち、約800万人が正規雇用されている。このうち、約600万人が正規雇用されている。このうち、約400万人が正規雇用されている。

スアエノールエチ(アロビ)レンオキシド変性ジ(×
タ)アクリレート、(×タ)アクリル化エポキシ樹脂、

[illegible]

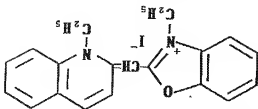
10 一ト、4-エチルフェニル(×タ)アリレート、ナフ
 テンエチル(×タ)アリレート、ナフテンエチル(×タ)アリレートなど
 の芳香環を含有する(×タ)アリレート化合物、芳香

[illegible]

*【0020】本発明で使用する一般式(1)で表わされるシアニン色素の代表例として、化合物(a)ないし化

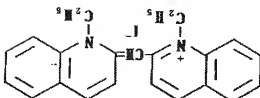
【0021】化合物(a)

[22]



【0022】化合物(b)

【123】

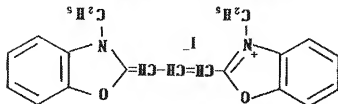


【0023】化合物(c)

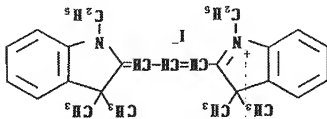
【化4】

とができる。この様な一般形式で表されるモノマーは、G. E. Fickes, K. Venkataraman¹⁾「The Chemistry of Synthetic Dyes」(第4巻、211~340頁(1971年)に記述の方法に従い合成することができ、また、(株)日本感光化学研究所から入手することもできる。

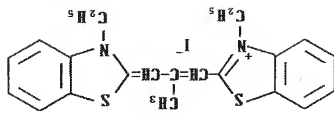
* 20

[illegible]

【0024】化合物(D)

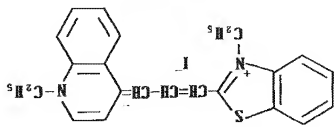


【0025】化合物(e)



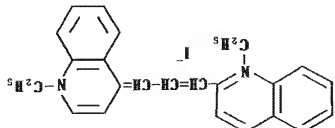
☆ ☆ 【化7】

【0026】化合物(f)



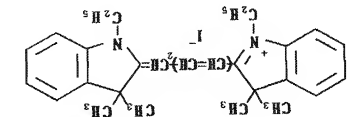
* * [化8]

【0027】化合物 (8)



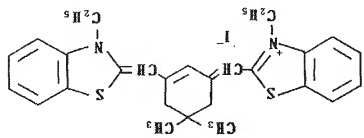
※ ※ [化9]

【0028】化合物 (9)



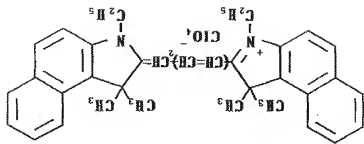
* * [化10]

【0029】化合物 (1)



☆ ☆ [化11]

【0030】化合物 (J)



◆ ◆ [化12]

【0031】化合物 (K)

13

* 〇〇〇〇豆類〇〇〇〇 *


スルホニウム有機ホウ素錯体が、シアニン色素(C)によつて効果的に光増感分解されることが要求されるが、R³、R⁴およびR⁵の内、少なくとも一つに、置換基

[illegible]

り、且つ、これらの基が優先的且つ効率的にアルホニウ
 人またはオキソアルホニウムカチオンから分解する性質
 を帯びることによって、フリーラジカルの発生効率が意


【0038】具体的な化合物(1)ないし化合物(r)となるからである。

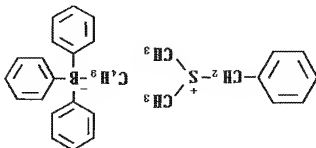
【0039】化合物(1)
【化14】

[O-]c1ccc(cc1)C2=CC=CC=C2

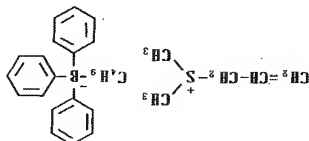
1-phenyl-2-vinyl-3-methyl-5-pyrazolone

【515】※



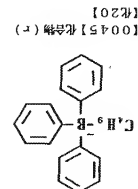


【0043】化合物(p)

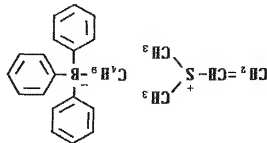


* 10* 【化18】

20* 【0045】化合物(r)

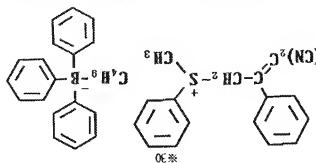


【化20】



【0044】化合物(q)

【化19】



※ 30

【0046】本発明で使用するホログラム記録用感光材料 40*も1個以上有する化合物(B)の屈折率と屈折率差が0.005以上であることが好ましく、さらに屈折率差が0.02以上であることがより好ましい。上記各成分の配合比に特定の制限はないが、照射用レーザー光の透過率が1%以上となるようにアズイン色素(C)の濃度を調整することが好ましい。さらに必要に応じて、各種添加剤、例えば可塑剤、連鎖移動剤、酸化防止剤、熱重分解防止剤、レバリン剤等を添加してもよい。

【0047】ビニモノマーの単一重合体または2成分以上のビニモノマーの共重合体である高分子化合物(A)の全感光材料中に占める量は、高回折効率を有する屈折率と、重合可能なエチレン性不飽和結合を少なくとも50

は、ビニモノマーの単一重合体または2成分以上のビ

重合可能なエチレン性不飽和結合を少なくとも1個以上有

する化合物(B)、およびアズイン色素(C)とアルホ

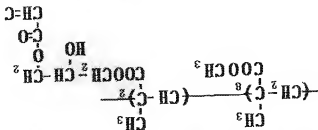
ニウム有機ホリ素結晶(D)からなる光重合開始剤を、

任意の濃度で適当な溶媒中に溶解させ、得られた溶液を

が、ビニモノマーの単一重合体または2成分以上の

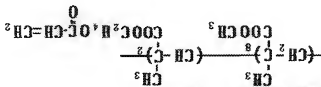
ビニモノマーの共重合体である高分子化合物(A)の

* 【0066】化合物(1)
【化22】



※他は、実施例20と同様の方法で操作した時の、感度特性、回折効率、アレバック波長及び保存安定性試験結果を表3に示した。

【0068】化合物(u)
【化23】



実施例27におけるPMMMAを、メチルメタクリレートと2-ヒドロキシエチルメタクリレートとのモル比で8対2の共重合体に、アリル酸クロライドをジメチルホルムアミド中、酸触媒存在下、室温で反応させ、アリロリル基を導入した高分子化合物(化合物(u))に替え※

果を表3に示した。

他は、実施例20と同様の方法で操作した時の、感度特

性、回折効率、アレバック波長及び保存安定性試験結

*

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*非変性アクリリートをペンタエリスリトールトリアクリレート替えた他は、実施例20と同様の方法で操作し、感度特性、回折効率、アレバック波長及び保存安定性試験結果を表3に示した。

【0072】実施例31

実施例28におけるポリ(α-プロモフェニルメタクリ

レート)を、アクリレンと無水マレイン酸とのモル比で9

対1の共重合体に、2-ヒドロキシエチルアクリレート

をトルエン中、ジメチルアニリンを触媒に用い、酸触媒

存在下、60℃で反応させ、アリロリル基を導入した高

分子化合物(化合物(v))に替えた他は、実施例28

と同様の方法で操作した時の、感度特性、回折効率、ア

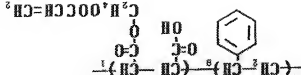
レバック波長及び保存安定性試験結果を表3に示し

【0070】実施例29
実施例28におけるポリ(α-プロモフェニルメタクリレート)をポリ(スチレン)に替えた他は、実施例28と同様の方法で操作した時の、感度特性、回折効率、アレバック波長及び保存安定性試験結果を表3に示した。

【0071】実施例30
実施例20におけるPMMMAをポリ(α-ナフチルアス

*

【化24】



☆ 【表1】

【0074】

【0075】保存性1は、25℃、60%RH保存下における耐久性を示す。保存性2は、90℃保存下における耐久性を示す。

【0076】

【表2】

50

試料	シエタン色素 (C)	スルホニウム 有機材料層 (D)	高分子 化合物 (A)	重合性 モノマー (B)	記録波長 (nm)	露光量 (mJ/cm ²)	回折効率 (%)	シエタン色素 波長 (nm)	保存性1 (B)	保存性2 (B)
1	化合物 (a)	化合物 (1)	PMMA	"	488	12	70	483	>180	>7
2	化合物 (b)	"	"	"	514	15	70	510	>180	>7
3	化合物 (c)	"	"	"	488	10	70	483	>180	>7
4	化合物 (d)	"	"	"	514	15	70	510	>180	>7
5	化合物 (e)	"	"	"	514	12	70	510	>180	>7
6	化合物 (f)	"	"	"	633	10	70	628	>180	>7
7	化合物 (g)	"	"	"	647	15	70	640	>180	>7
8	化合物 (h)	"	"	"	633	10	70	628	>180	>7
9	化合物 (i)	"	"	"	647	12	70	640	>180	>7
10	化合物 (j)	"	"	"	678	8	70	672	>180	>7
11	化合物 (k)	"	"	"	633	12	70	628	>180	>7

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(13)

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試験例	シニアジド系 (C)	スルホニウム 青酸4-置換体 (D)	高分子 化合物 (A)	割合性 モノマー (B)	記録線長 (m)	露光量 (mJ/cm ²)	露光時間 (s)	フレイバインク 線長 (m)	保存性1 (B)	保存性2 (B)
12	化合物 (c)	化合物 (m)	PMMA	コポリメリチレン-1	488	10	70	483	>180	>7
13	"	化合物 (n)	"	"	488	10	70	483	>180	>7
14	"	化合物 (o)	"	"	488	25	70	483	>180	>7
15	"	化合物 (p)	"	"	488	30	70	483	>180	>7
16	"	化合物 (q)	"	"	488	30	70	483	>180	>7
17	"	化合物 (r)	"	"	488	25	70	483	>180	>7

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(14)

時間平6-175565
26
【0077】保存性1は、25℃、60%RH保存下における耐久性を示す。保存性2は、90℃保存下における耐久性を示す。
【0078】
【表3】

【0079】保存性1は、25℃、60%RH保存下における耐久性を示す。保存性2は、90℃保存下における耐久性を示す。

【0080】
 【発明の効果】本発明に依り、広い波長領域に渡って高感度で、化学的に安定であり、かつ溶解度、高回折効率、高透明性を有する体積位相型ホログラムを簡便に製造することが可能となる。

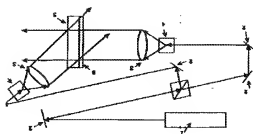
* 50
 2：ミラー
 1：レーザ発振装置
 【符号の説明】
 【0081】図1は、ホログラム作成用二光束露光装置のブロック図を示す。

【図面の簡単な説明】
 【0082】図1は、ホログラム作成用二光束露光装置

波長 (nm)	照射光の波長 (nm)	照射光の強度 (mJ/cm ²)	照射光の波長 (nm)	照射光の強度 (mJ/cm ²)	照射光の波長 (nm)	照射光の強度 (mJ/cm ²)	照射光の波長 (nm)	照射光の強度 (mJ/cm ²)	照射光の波長 (nm)	照射光の強度 (mJ/cm ²)
1.8	1.8	1.0	1.8	1.0	1.8	1.0	1.8	1.0	1.8	1.0
2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7	2.7
2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9
3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1

5:ガラス板
6:感光膜

3:レンズ
4:スベリシヤルワイルダー



【図1】

フロントページの書き

技術表示箇所

識別記号 序内整理番号 FI

(51) Int. Cl. 5
G03F 7/038

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacturing method of a simple volume phase type hologram using the hologram recording material and it which were excellent in chemical stability or an environmental capability-proof, and had a high sensitivity characteristic in the large wavelength area, and were excellent in resolution, diffraction efficiency, and transparency.

[0002]

[Description of the Prior Art] Conventionally, generally the photosensitive materials of a bleaching processing silver salt and a dichromated gelatin system have been used as a charge of hologram recording material. However, both the hologram materials using this needed complicated wet-developing processing, and it had the problem of being further inferior to resolution or an environmental capability-proof, for example, moisture resistance, and weatherability.

[0003] The hologram recording material using a photopolymer is proposed that such a problem should be solved. For example, in JP,62-22152,B, the hologram recording material characterized by the polyfunctional monomer which has two or more ethylenic unsaturated bonds, the polymer of non-cross-linking, and combination with an initiator is indicated. If the known art concerned is followed, can manufacture the hologram outstanding in points, such as diffraction efficiency, resolution, and an environmental capability-proof, but, it had a fault, like problems, such as development unevenness which originates in the manufacturing complicated nature of having adopted the wet process process in manufacture of a hologram and the opening produced at the time of solvent immersion operation, or a crack or it is inferior to the sensitivity characteristic in a long wavelength field, and a fall of the transparency by a white bluish mark, arise. Since the polymer used was non-cross-linking, there was a fault of

being inferior to the intensity of a hardening layer.

[0004] The hologram recording material (and) using the photopolymer which can manufacture a hologram only by interference exposure on the other hand as only down stream processing which does not need a complicated or complicated wet process process in the manufacturing process of a hologram, or its manufacturing method is indicated. For example, in JP,2-3081,A or JP,2-3082,A, The photopolymerization nature constituent for hologram recording and the element for refractive-index pictures which comprise thermoplastic polymer having a substituent in which either polymer or a monomer contains an aromatic ring or a halogen atom, a fluid ethylenic monomer, and a photoinitiator are indicated. That the hologram excellent in high diffraction efficiency, high resolution, an environmental capability-proof, and transparency will be manufactured if this known art is followed, SPIE "Practical Holography IV", the 12th and 25 volume, 30 pages (1990) and "Journal of Imaging Science", the 35th volume, 19 pages, and 25 pages (1991) prove. However, the sensitivity characteristic in the long wavelength field of this hologram recording material is a several 100 mJ/cm² order.

In order to shorten exposure time in the duplicate of a hologram, to raise a sensitivity characteristic further was desired.

[0005] In JP,2-51188,A, the constituent for holograms which becomes the intramolecular which has a difference in a refractive index from the plurality of a compound which has one or more polymerization nature carbon-carbon double bonds is indicated. If this known art is followed, the high resolution and the hologram of high diffraction efficiency which do not need complicated down stream processing will be manufactured, but. Since urethane acrylate with a low glass transition temperature was used for intramolecular as one of the compounds which has one or more polymerization nature carbon-carbon double bonds, it had the fault that it was inferior in the heat resistance characteristics of a hologram.

[0006] In JP,3-36582,A and JP,3-249785,A, the hologram recording material combining the allyl monomer a refractive index and whose polymerization nature are different, and an acrylic monomer is indicated. If this known art is followed, it is proved by the "Holographic Display Artists and Engineers Club report", the 10th volume, No. 1, and 3 pages (1990) that the volume phase type hologram of high diffraction efficiency can be manufactured. However, in this known art, since the monomer which has mobility was used as the main ingredients, processing for controlling the mobility of a film, such as heat-treating before hologram exposure, needed to be performed beforehand, and operation became complicated and it had a fault, like control of thickness is difficult.

[0007]

[Problem(s) to be Solved by the Invention] This invention is providing the simple manufacturing method of a volume phase type hologram using a hologram recording material and it with the

characteristic which was excellent in the environmental capability-proof, and was excellent in high sensitivity and resolution, diffraction efficiency, and transparency in the large wavelength area.

[0008]

[Means for Solving the Problem] This invention persons result in this invention, as a result of inquiring wholeheartedly in consideration of the above many points that the above-mentioned purpose should be attained.

[0009] Namely, a high molecular compound (A) whose first invention is a homopolymer of a vinyl monomer, or a copolymer of two or more ingredients, it is a hologram recording material including combination of a compound (B) and cyanine dye (C) which have at least one or more ethylenic unsaturated bonds which can polymerize, and a sulfonium organically boron complex (D). The second invention is a hologram recording material given in the first invention for which a high molecular compound (A) which is a homopolymer of a vinyl monomer or a copolymer of two or more ingredients is characterized by having an acrylyl group (meta) which can construct a bridge. A refractive index of a high molecular compound (A) whose third invention is a homopolymer of a vinyl monomer, or a copolymer of a vinyl monomer of two or more ingredients, it is a hologram recording material given in the first invention, wherein refractive index difference with a refractive index of a compound (B) which has at least one or more ethylenic unsaturated bonds which can polymerize is 0.005 or more. A high molecular compound (A) whose fourth invention is a homopolymer of a vinyl monomer, or a copolymer of a vinyl monomer of two or more ingredients, A compound (B) which has at least one or more ethylenic unsaturated bonds

which can polymerize, either the first invention including combination of cyanine dye (C) and a sulfonium organically boron complex (D) or thru/or the third invention -- in creating a hologram using a hologram recording material of a statement, After carrying out hologram exposure of this hologram recording material, it is a manufacturing method of a volume phase type hologram applying light and (or) heat.

[0010] Hereafter, this invention is explained extensively.

[0011] First, a high molecular compound (A) which is a homopolymer of a vinyl monomer or a copolymer of a vinyl monomer of two or more ingredients used by this invention is illustrated. As a polymer of such a vinyl monomer, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, pentyl, Neopentyl one, hexyl, nonyl, dodecyl, 2-methylbutyl, 3-methylbutyl, 2-ethylbutyl, 1,3-dimethylbutyl, 2-ethylhexyl, 2-methylpentyl, cyclohexyl, adamantanyl, Chains, such as isobornyl, dicyclopentanyl, and tetrahydrofurfuryl, A letter of branching, and a polymer of acrylic ester monomer (meta) of annular alkyl, 2-hydroxyethyl, 2-hydroxypropyl, 4-hydroxybutyl, A polymer of acrylic ester monomer which has hydroxyl groups, such as glycerol, 2-hydroxy-3-phenoxypentyl, and 2-(meta) acryloyloxyethyl 2'-hydroxypropyl phthalate (meta),

Phenyl, 4-methoxy carbonylphenyl, 4-ethoxycarbonylphenyl, 4-butoxycarbonylphenyl, 4-tert-butylphenyl, benzyl, 4-phenylethyl, 4-phenoxydiethylene glycol, 4-phenoxytetraethylene glycol, A polymer of acrylic ester monomer (meta) containing aromatic rings, such as 4-phenoxyhexaethylene glycol and 4-biphenyl, A polymer of acrylic ester monomer (meta) containing epoxy groups, such as glycidyl (meta) acrylate, A polymer of acrylic ester monomer (meta) containing iron atoms, such as ferrocenyl-methyl group and ferrocenyl-ethyl group, Trifluoroethyl, tetrafluoro propyl, heptafluorodecyl, A polymer of acrylic ester (meta) containing halogen atoms, such as octafluoropropyl and 2,3-dibromopropyl, A polymer of acrylic ester (meta) containing alkoxyisilane groups, such as trimethoxysilylpropyl, A polymer of acrylic ester monomer (meta) containing amino groups, such as N,N-dimethylaminoethyl, a N,N-diethylaminoethyl, and t-butylamino ethyl, (Meta) Acrylic acid, itaconic acid, maleic acid, p-vinylbenzoic acid, 2-(meta) acryloyloxyethyl succinic acid, 2-(meta) acryloyloxyethyl phthalic acid, 2-(meta) acryloyloxypropyl phthalic acid, A polymer of a vinyl monomer containing carboxyl groups, such as 2-(meta) acryloyloxypropyl tetrahydrophthal acid and 2-(meta) acryloyloxypropyl hexahydrophthalic acid, A polymer of phosphate group content (meta) acrylic ester monomer, such as ethyleneoxide denaturation phosphoric acid (meta) acrylate, Acrylamide, N-butylacrylamide, N,N-dimethylacrylamide, Acrylonitrile, styrene, 4-hydroxystyrene, 4-hydroxymethylstyrene, 4-bromostyrene, chloromethyl styrene, perfluoro styrene, Alpha-methylstyrene, vinyltoluene, vinyl acetate, VC/M/PVC, a vinylidene chloride, A polymer of vinyl monomers, such as N-vinyl pyrrolidone, N-vinylcarbazole, vinylpyridine, vinylpyrrolidone, vinylbutyral, and a vinyl acetal, is mentioned, and these copolymers of two or more ingredients are mentioned.

[0012]Next, as a high molecular compound which has an acrylyl group (meta) which can construct a bridge with a homopolymer of a vinyl monomer or a copolymer of a vinyl monomer of two or more ingredients used in this invention, it is obtained by introducing an acrylyl group (meta) into a high molecular compound which contains as a unit a vinyl monomer which has functional groups, such as a hydroxyl group, a carboxyl group, a phosphate group, a chloromethyl group, or an epoxy group, among polymers of said vinyl monomer. Such a reactive polymer, for example functional polymer series "reactive polymer", Yoshio Iwakura, the Kurita ***** Kodansha SAIENTIFIKU (1977). Or it is compoundable by a method indicated to functional series "photosensitive polymers", Gentaro Nagamatsu, ***** and Kodansha SAIENTIFIKU (1977).

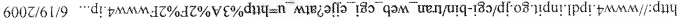
[0013]As a compound (B) which has at least one or more polymerization nature ethylenic unsaturated bonds of use by this invention, oligomer other than monofunctional or a polyfunctional vinyl monomer may be included, and it may be the amount compound of polymers further. Next, these compounds are illustrated.

[0014](Meta) Unsaturated acid compounds, such as acrylic acid, itaconic acid, and maleic

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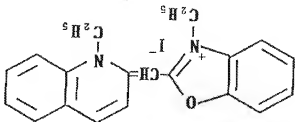
a sulfur atom. Express a selenium atom, an NH group, a CH=CH basis, or C(CH₃)₂ set, and n is shown, and integers, such as 0, 1, or 2, R¹ and R², Mutually, an alkyl group, a substituted alkyl group, an aryl group, a substitution aryl group, an aralkyl group, or an alkenyl group is shown, and it may be the same, or may differ, and X, Halogen, NO₂, BF₄⁻, PF₆⁻, AsF₆⁻, ClO₄⁻, SbF₆⁻, CF₃SO₃, CH₃SO₃, or CH₃C₆H₄SO₃ is shown. The cyanine dye (C) expressed is mentioned.

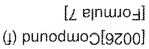
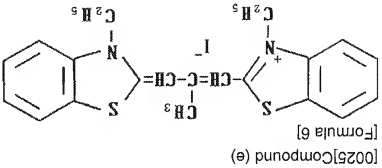
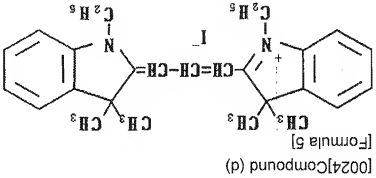
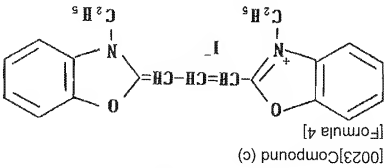
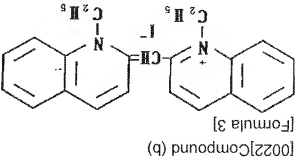
[0018]Next, if a substituent in a general formula (1) is explained, as an alkyl group which may have a substituent, A methyl group, an ethyl group, n-butyl group, a sec-butyl group, a tert-butyl group, A pentyl group, a hexyl group, an octyl group, a decyl group, dodecyl, an octadecyl group, A stearyl group, a cyclohexyl group, a menthyl group, a bornyl group, benzyl, An acetoxy group, a phenacyl group, a salicyl group, an anisyl group, a cyanomethyl group, A chloromethyl group, a bromomethyl group, a methoxy carbonylmethyl group, an ethoxy carbonylmethyl group, A chloromethyl group, a bromomethyl group, a trifluoromethyl group, a carbonylmethyl group, As an aryl group which are a methoxymethyl group, a carboxymethyl group, a hydroxymethyl group, a menthyl group, the Pina Nils group, etc., and may have a substituent, A phenyl group, p-tolyl group, a xylol group, a mesityl group, a KUMENIRU group, p-methoxyphenyl group, a biphenyl group, a naphthyl group, an anthryl group, They are a phenan tolyl group, p-cyanophenyl group, a 2,4-bis(trifluoromethyl)phenyl group, p-fluorophenyl group, p-chlorophenyl group, p-dimethylaminophenyl group, p-phenylthiophenyl group, etc., As an alkenyl group, a carbon number can express an alkenyl group of linear shape to 2 thru/ or 4, or a letter of branching, and can mention a vinyl group, an allyl group, 1-propenyl group, 2-butenyl group, 3-butenyl group, an isopropenyl group, etc.

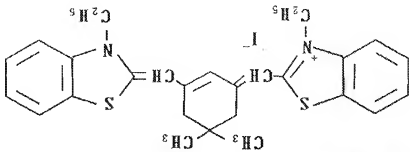
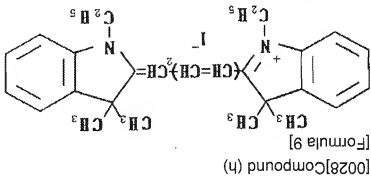
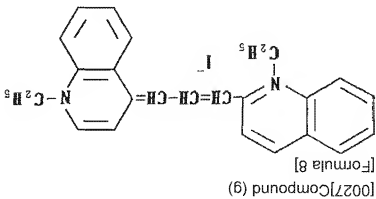
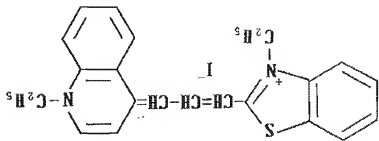
[0019]Cyanine dye expressed with such a general formula (1), G.E. Ficken, volume [4th] "The Chemistry of Synthetic Dyes" [edited by KVenkataraman], it can compound [211-340 pages (1971)] in accordance with a method of a statement, and can also obtain from Japanese Sensitizing dye research institute.

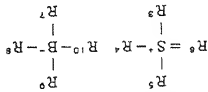
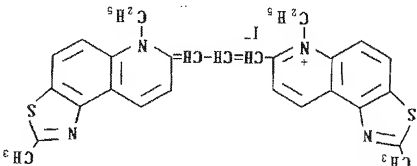
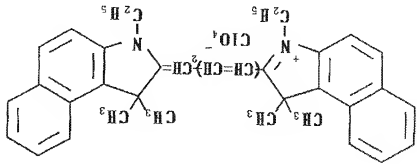
[0020]As an example of representation of cyanine dye expressed with a general formula (1) used by this invention, a compound (a) thru/ or a compound (k) are shown below.

[0021]Compound (a)
[Formula 2]









(Independently R^3 in a formula, R^4 , and R^5 , respectively) The alkyl group which may have a substituent, the aryl group which may have a substituent, The alkenyl group which may have a substituent, the alkyne group which may have a substituent, The alicycle group which may have a substituent, the alkoxy group which may have a substituent, The aryloxy group which may have a substituent, the alkylthio group which may have a substituent, and the amino group which may have a substituent, R^6 an oxygen atom or a lone-pair electrons R^7 , R^8 , The alkyl group in which R^9 and R^{10} may have a substituent independently, respectively, The aryl group which may have a substituent, the alkenyl group which may have a substituent, The basis chosen from the alkyl group which may have a substituent is shown, and R^3 , R^4 and R^5 may be cyclic

structures which the two or more basis has combined, do not serve as an aryl group in which R³, R⁴, and R⁵ may have a substituent simultaneous [two or more], and R⁷, R⁸, All R⁹ and R¹⁰ do not serve as an aryl group which may have a substituent simultaneously. The

sulfonium organically boron complex chosen from the sulfonium organically boron complex or oxo sulfonium organically boron complex expressed is shown. The sulfonium organically boron complex expressed with a general formula (2) is [Japanese Patent Application No. / No. 56831 / four to] compoundable in accordance with the method of a statement.

[0034] in substituent R³ on sulfonium in a general formula (2), or an oxo sulfonium cation, R⁴, and R⁵, As an alkyl group which it may have, a substituent A methyl group, an ethyl group, a tert-propyl group, An isopropyl group, a butyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, A pentyl group, a hexyl group, an octyl group, a decyl group, dodecyl, an octadecyl group, An allyl group, benzyl, an acetonyl group, a phenacyl group, a salicyl group, An anisyl group, a cyanomethyl group, a chloromethyl group, a bromomethyl group, a methoxycarbonylmethyl group, An ethoxycarbonylmethyl group, a menthyl group, the Fina Nils group, etc. as an aryl group which may have a substituent, A phenyl group, p-tolyl group, a xyllyl group, a mesityl group, a KUMENIRU group, p-methoxyphenyl group, a biphenyl group, a naphthyl group, an anthryl group, A phenan tolyl group, p-cyanophenyl group, a 2,4-bis(trifluoromethyl)phenyl group, p-fluorophenyl group, p-chlorophenyl group, p-

dimethylaminophenyl group, p-phenylthiophenyl group, etc. as an alkenyl group which may have a substituent A vinyl group, 1-propenyl group, 1-butenyl group, a 3,3-dicyano 1-propenyl group, etc. as an alicycle group which may have a substituent, A cyclopentyl group, a cyclohexyl group, a norbornyl group, a bornyl group, 1-cyclohexenyl group etc. as an alkoxy group which may have a substituent A methoxy group, A tert-butoxy group, a benzyloxy group, etc. as an aryloxy group which may have a substituent, A phenoxy group, p-tolyloxy group, p-fluorophenoxy group, p-nitro phenoxy group, etc. as an alkylthio group which may have a substituent, A methylthio group, an ethyl thio group, a butyl thio group, etc. as an arylthio group which may have a substituent, A phenylthio group, p-tolyl thio group, p-cyano phenylthio group, etc. as an amino group which may have a substituent, An amino group, a methylamino group, a dimethylamino group, a cyclohexylamino group, An anilino group, a piperidino group, a morpholino group, etc. are mentioned, and further R³, An alkylene group which R⁴ and R⁵ may be cyclic structures which the two or more basis has combined, for example, may have substituents, such as a tetramethylen group, a pentamethylene group, and a 1,4-dichlorotetramethylen group, Although an ethylene dioxy group, a diethylenedioxy group, a horse mackerel POIRU group, ethylene dithio, etc. are mentioned, this invention is not limited to these.

[0035] in substituent R⁷, R⁸, R⁹, and R¹⁰ on an organic boron anion in a general formula (2),

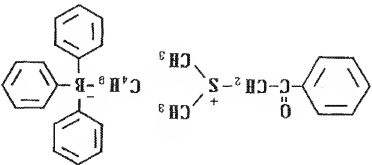
As an alkyl group which it may have, a substituent A methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, a pentyl group, a hexyl group, an octyl group, a decyl group, a dodecyl, an octadecyl group, an allyl group, benzyl, etc. as an aryl group which may have a substituent, A phenyl group, p-tolyl group, a xylyl group, a mesityl group, a KUMENIRU group, p-methoxyphenyl group, a naphthyl group, a 2,4-bis(trifluoromethyl)phenyl group, p-fluorophenyl group, p-chlorophenyl group, p-bromo phenyl group, etc. as an alkenyl group which may have a substituent, As an alkynyl group in which a vinyl group, 1-propenyl group, 1-butenyl group, etc. may have a substituent, although an ethenyl group, a 2-tert-butylethenyl group, 2-phenylethenyl group, etc. are mentioned, this invention is not limited to these.

[0036] In a general formula (2), as a desirable structure, especially, R^3 , R^4 , and R^5 , at least one. An allyl group which may have a substituent, benzyl which may have a substituent, it is the structure which is either a vinyl group which may have a substituent, or a phenacyl group which may have a substituent, is an alkyl group in which R^7 may have a substituent, and is an aryl group in which R^8 , R^9 , and R^{10} may have a substituent.

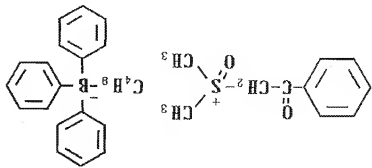
[0037] Although it is required that photosensitization decomposition of the sulfonium organicity boron complex shown by a general formula (2) should be effectively carried out with cyanine dye (C) as this reason, To at least one of R^3 , R^4 , and R^5 . By introducing an allyl group which may have a substituent, benzyl which may have a substituent, a vinyl group which may have a substituent, or a phenacyl group which may have a substituent, By being tinged with character which the electronic receptiveness of a polymerization initiator shown by a general formula (2) increases, and these bases decompose from sulfonium or an oxo sulfonium cation preferentially and efficiently, it is because it becomes possible to think that generating efficiency of a free radical increases and to aim at improvement in sensitivity as a result.

[0038] A concrete compound (i) thru/or a compound (r) is shown below.

[Formula 14]

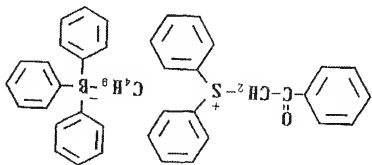


[0040] Compound (m)
[Formula 15]



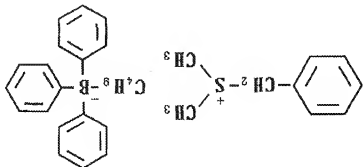
[0041]Compound (n)

[Formula 16]



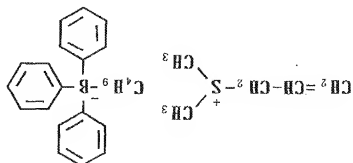
[0042]Compound (o)

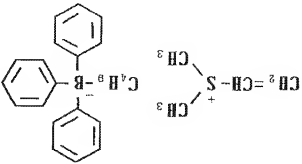
[Formula 17]



[0043]Compound (p)

[Formula 18]





[0047]Quantity occupied in all the photosensitive materials of a high molecular compound (A)

which is a homopolymer of a vinyl monomer or a copolymer of a vinyl monomer of two or more ingredients is 30 to 70 % of the weight preferably ten to 90 % of the weight, in order to perform hologram recording which has high diffraction efficiency. The amount of compound (B) used which has at least one or more ethylenic unsaturated bonds which can polymerize, it is 40 - 150 weight section preferably ten to 200 weight section to high molecular compound (A) 100 weight section which is a homopolymer of a vinyl monomer or a copolymer of high diffraction of two or more ingredients which is a base material. Since maintenance of high diffraction efficiency and improvement in a sensitivity characteristic will become difficult if it deviates from a mentioned range, it is not desirable.

[0048]Cyanine dye (C) of a general formula (1) among photopolymerization initiators of use by this invention, it is preferably used in the range of 0.5 - 15 weight section 0.1 to 30 weight section to high molecular compound (A) 100 weight section which is a homopolymer of a vinyl monomer, or a copolymer of two or more ingredients. The amount used receives restriction with optical density of photosensitive layer thickness and this thickness. That is, it is preferred that optical density uses it in the range which does not exceed 2. A sulfonium organically boron complex (D) is preferably used in the range of 1 - 15 weight section 0.1 to 20 weight section to high molecular compound (A) 100 weight section which is a homopolymer of a vinyl monomer, or a copolymer of two or more ingredients.

[0049]A film is formed on substrates, such as a direct glass plate and a plastic film, by using a sensitizing solution made to dissolve hologram recording photosensitive materials of the above composition ratios in a suitable solvent for a spin coater, a roll coater, a knife coating machine, or a bar coating machine. A protective layer for oxygen interception may be formed on it. A protective layer may paste together a film or boards made from a plastic, such as polyethylene, polyvinyl chloride, a polyvinylidene chloride, polyvinyl alcohol, or polyethylene terephthalate, or may carry out coating of the solution of said polymer. A glass plate may be pasted together, in order to improve airtightness between a protective layer and a film (and) or between a substrate and a film, a binder or a liquefied substance may be made to exist.

[0050]A sensitive plate or a film formed above with hologram recording photosensitive materials produced by making it like, After fixing to an electrode holder so that it may not be influenced by vibration, it irradiates with visible light laser, such as helium-Cd laser, Ar ion laser, helium-Ne laser, Kr ion laser, and ruby laser, and volume phase type hologram record is performed. An example of an optical system is shown in drawing 1.

[0051]A sensitive plate or a film by which hologram recording was carried out needs to apply light and (or) heat for fixing of an unexposed portion or a portion with few light exposures. Visible light and (or) ultraviolet radiation, such as a carbon arc, a high-pressure mercury-vapor lamp, a xenon lamp, a metal halide lamp, a fluorescent lamp, a tungsten lamp, etc. besides

visible light laser, are used for light. As for heat, heating among 40 to 160 °C is preferred. Light and heat may be simultaneously applied to a sensitive plate or a film by which hologram recording was carried out, or light and heat may be applied independently. Operation of exciting a protective film before and after applying light and (or) heat may be performed. [Function] The high molecular compound (A) whose hologram recording material of use by this invention is a homopolymer of a vinyl monomer, or a copolymer of the vinyl monomer of two or more ingredients. The combination of the compound (B) and cyanine dye (C) which have at least one ethylenic unsaturated bond which can polymerize, and a sulfonium organically boron complex (D) is included.

[0052] In [if the hologram recording material of this photopolymerization nature is irradiated with a laser beam in hologram recording] the strong part of this interferential action in a laser radiation part. The compound (B) which has at least one or more ethylenic unsaturated bonds where the polymerization reaction of the compound (B) which has at least one or more ethylenic unsaturated bonds which can polymerize arises, which are in the weak part of interferential action in that case, and which can be polymerized spreads and polymerizes to the strong part of the interferential action of this laser beam. Therefore, in the strong part of the interferential action of this laser beam, density improves compared with the weak part of interferential action, as a result, among both parts, refractive index difference arises and a hologram is recorded. The refractive index of the high molecular compound (A) which is a homopolymer of a vinyl monomer, or a copolymer of the vinyl monomer of two or more ingredients at this time, When refractive index difference with the refractive index of the compound (B) which has at least one or more ethylenic unsaturated bonds which can polymerize is 0.05 or more, the refractive index difference of the strong part of the interferential action of this laser beam and a weak part becomes large, and it is guessed that the volume phase type hologram with high diffraction efficiency was manufactured. Furthermore, after hologram recording, by adding the light and (or) heat, the polymerization of the compound (B) which has at least one or more ethylenic unsaturated bonds in which the unreacted polymerization is possible is promoted, it is chemically stable and a hologram without aging is manufactured. In the case where the high molecular compound (A) which is a homopolymer of a vinyl monomer or a copolymer of the vinyl monomer of two or more ingredients has an acrylyl group (meta) which can construct a bridge at this time, Crosslinking reaction arises between (A) and (B), it is still more chemically stable and a hologram without aging is manufactured. The cyanine dye (C) which remained as a coloring component is effectively decolorized by down stream processing, especially optical exposure, and the transparency of a hologram is made to improve by them after this.

[0053]

[Example] Based on an example, this invention is explained more to details below. In each

following example, especially, a part expresses a weight section, as long as there is no notice. Example 1 - 11 poly methyl methacrylate (PMMA) 100 weight sections. The cyanine dye (compound (a)) thru/or the compound (k) expressed with 90 copies and a general formula (1) in phenoxy ethyl acrylate (POEA) Three copies, On a 100X125X3-mm glass plate, the sensitizing solution which consists five copies and tetrachloroethane of 900 copies in a sulfonium organically boron complex (compound (l)) was applied using a 3-mil applicator so that the thickness after sensitizing solution desiccation might be set to 10 micrometers, and the sensitive plate for hologram recording was created. The 5-% of the weight solution of polyvinyl alcohol was applied by a 3-mil applicator. Hologram exposure by two beam interference was performed to this sensitive plate using the optical system for hologram creation shown in drawing 1. In Examples 1 and 3, the 488-nm light of Ar ion laser is used in that case, in Examples 2, 4, and 5, the 514-nm light of Ar ion laser is used, in Examples 6, 8, and 11, the 676-nm light of Kr ion laser was used in Example 10 using the 647-nm light of Kr ion laser in Examples 7 and 9 using the 633-nm light of helium-Ne laser. After carrying out hologram exposure, one side of 2 light flux was intercepted and it exposed to the same exposure time as [0054D]Diffraction efficiency was measured with the product ARTmade from Jasco Industry25C type spectrophotometer. This device can install a photograph millimeter with a 3-mm-wide slit on the circumference with a radius [centering on a sample] of 20 cm. 0.3-mm-wide monochromatic light was entered into the sample at the angle of 45 degrees, and the diffracted light from a sample was detected. The ratio of the biggest value except regular reflection light and a value when a sample is not placed but direct incident light is received was made into diffraction efficiency. The exposure energy quantity which gives the maximum diffraction efficiency, diffraction efficiency, playback wavelength, and a preservation stability test result were collectively shown in Table 1.

[0055]Replaced the sulfonium organically boron complex (l) in 12 to example 17 Example 3 with the sulfonium organically boron complex (compound (m)) thru/or the compound (r), and also. A sensitivity characteristic, diffraction efficiency, playback wavelength, and a preservation stability test result when it was operated by the same method as Example 3 were shown in Table 2.

[0056]A sensitivity characteristic, diffraction efficiency, playback wavelength, and a preservation stability test result when the monomer in example 18 Example 3 which can be polymerized was changed to tetrabromobisphenol A ethylene oxide denaturation dimethacrylate and also it was operated by the same method as Example 3 were shown in Table 3.

[0057]A sensitivity characteristic, diffraction efficiency, playback wavelength, and a preservation stability test result when the monomer in example 19 Example 3 which can be

polymerized was changed to N-vinylcarbazole and also it was operated by the same method as Example 3 were shown in Table 3.

[0058] A sensitivity characteristic, diffraction efficiency, playback wavelength, and a preservation stability test result when the monomer in example 20 Example 3 which can be polymerized was changed to tribromo FENORUTORI ethylene oxide denaturation acrylate and also it was operated by the same method as Example 3 were shown in Table 3.

[0059] A sensitivity characteristic, diffraction efficiency, playback wavelength, and a preservation stability test result when the monomer in example 21 Example 3 which can be polymerized was changed to ferrocenyl-ethyl group methacrylate and also it was operated by the same method as Example 3 were shown in Table 3.

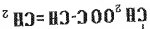
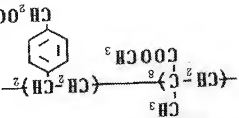
[0060] A sensitivity characteristic, diffraction efficiency, playback wavelength, and a preservation stability test result when PMMA in example 22 Example 20 was changed to poly (isobornyl methacrylate) and also it was operated by the same method as Example 20 were shown in Table 3.

[0062] A sensitivity characteristic, diffraction efficiency, playback wavelength, and a preservation stability test result when PMMA in example 24 Example 20 was changed to poly (vinyl acetate) and also it was operated by the same method as Example 20 were shown in Table 3.

[0063] For PMMA in example 25 Example 20, acrylic acid potassium to eight-pair a copolymer two by the mole ratio of methyl methacrylate and chloromethyl styrene The inside of dimethylformamide, A sensitivity characteristic, diffraction efficiency, playback wavelength, and a preservation stability test result when it changed to the formation of oxygen existence and the high molecular compound (compound (s)) which made it react at 60 ° and introduced the AKURIRORIRU group and also was operated by the same method as Example 20 were shown in Table 3.

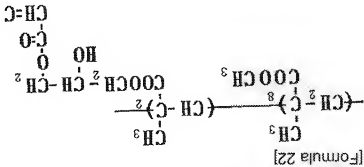
[0064] Compound (s)

[Formula 21]



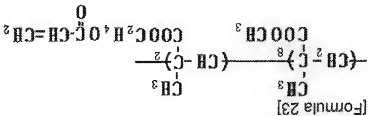
[0065]PMMMA in example 26 Example 20 by the mole ratio of methyl methacrylate and glycidyl methacrylate to eight-pair a copolymer two. Changed to the high molecular compound (compound (i)) which made acrylic acid react at the formation of oxygen existence, and 60 ** among toluene by having made dimethylaniline into the catalyst, and introduced the AKURIRORIRU group, and also. A sensitivity characteristic, diffraction efficiency, playback wavelength, and a preservation stability test result when it was operated by the same method as Example 20 were shown in Table 3.

[0066]Compound (i)



[0067]PMMMA in example 27 Example 20 by the mole ratio of methyl methacrylate and 2-hydroxyethyl methacrylate to eight-pair a copolymer two. Changed to the high molecular compound (compound (ii)) which oxygen-existence-izes acrylic acid chloride among dimethylformamide, made it react at a room temperature, and introduced the AKURIRORIRU group, and also. A sensitivity characteristic, diffraction efficiency, playback wavelength, and a preservation stability test result when it was operated by the same method as Example 20 were shown in Table 3.

[0068]Compound (ii)



[0069]PMMMA in example 28 Example 20 to poly (p-bromophenyl methacrylate). A sensitivity characteristic, diffraction efficiency, playback wavelength, and a preservation stability test result when tribromo FENORUTORI ethyleneoxide denaturation diacrylate was changed to trifluoroethyl acrylate and also it was operated by the same method as Example 20 were shown in Table 3.

[0070]A sensitivity characteristic, diffraction efficiency, playback wavelength, and a

preservation stability test result when poly (p-bromophenyl methacrylate) in example 29

Example 28 was changed to poly (styrene) and also it was operated by the same method as

Example 28 were shown in Table 3.

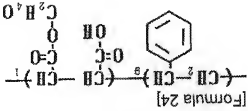
[0071] PMMA in example 30 Example 20 to poly (alpha-naphthyl styrene). tribromo
FENORUTORI ethyleneoxide denaturation diacrylate -- pentaerythritol -- doria -- KURIRETO
***** showed a sensitivity characteristic, diffraction efficiency, playback wavelength, and a

preservation stability test result when it was operated by the same method as Example 20 in

Table 3.

[0072] Poly (p-bromophenyl methacrylate) in example 31 Example 28. To the copolymer of 9 to
1, 2-hydroxyethyl acrylate by the mole ratio of styrene and a maleic anhydride The inside of
toluene. Used dimethylaniline for the catalyst, it was made to react at the formation of oxygen
existence, and 60 **, and a sensitivity characteristic, diffraction efficiency, playback
wavelength, and a preservation stability test result when it changed to the high molecular
compound (compound (v)) which introduced the AKURIORIRU group and also was operated
by the same method as Example 28 were shown in Table 3.

[0073] Compound (v)



[0074]

[Table 1]

実施例	シニアソ色素 (C)	スルホニウム 有機色素精体 (D)	高分子 化合物 (A)	重合性 モノマー (B)	記録波長 (nm)	露光量 (mJ/cm ²)	回折効率 (%)	プレイバック 波長 (nm)	保存性 1 (日)	保存性 2 (日)
1	化合物 (a)	化合物 (1)	PMMA	"	488	12	70	483	>180	>7
2	化合物 (b)	"	"	"	514	15	70	510	>180	>7
3	化合物 (c)	"	"	"	488	10	70	483	>180	>7
4	化合物 (d)	"	"	"	514	15	70	510	>180	>7
5	化合物 (e)	"	"	"	514	12	70	510	>180	>7
6	化合物 (f)	"	"	"	633	10	70	628	>180	>7
7	化合物 (g)	"	"	"	647	15	70	640	>180	>7
8	化合物 (h)	"	"	"	633	10	70	628	>180	>7
9	化合物 (i)	"	"	"	647	12	70	640	>180	>7
10	化合物 (j)	"	"	"	676	8	70	672	>180	>7
11	化合物 (k)	"	"	"	633	12	70	628	>180	>7

[0075]The preservability 1 shows the endurance under 25 ** and 60%RH preservation. The preservability 2 shows the endurance under 90 ** preservation.

[Table 2]

実態例	ソートン色素 (C)	スルホニウム 有機材料液体 (D)	高分子 化合物 (A)	重合性 モノマー (B)	記録線長 (nm)	露光量 (mJ/cm ²)	回折効率 (%)	デレイベータ 長さ (nm)	保存性 1 (日)	保存性 2 (日)
1 2	化合物 (c)	化合物 (m)	PMA	"	488	10	70	483	>180	>7
1 3	"	化合物 (n)	"	"	488	10	70	483	>180	>7
1 4	"	化合物 (o)	"	"	488	25	70	483	>180	>7
1 5	"	化合物 (p)	"	"	488	30	70	483	>180	>7
1 6	"	化合物 (q)	"	"	488	30	70	483	>180	>7
1 7	"	化合物 (r)	"	"	488	25	70	483	>180	>7

[0077]The preservability 1 shows the endurance under 25 ** and 60%RH preservation. The preservability 2 shows the endurance under 90 ** preservation.

[0078]

[Table 3]

実施例	シニチン色素 (C)	染料溶液 (D)	高分子化合物 (A)	化 合 物 (B)	重合反応 (mm)	重合温度 (°C)	固形分率 (%)	フレイク径 範囲 (mm)	粒径1 (μm)	粒径2 (μm)
18	化合物 (c)	化合物 (1)	PMMA	3,3',5,5'-四(4-tert-butylphenyl)-4,4'-二(2,2,6,6-テトラメチル-5-ヒドロキシ-1,4-ベンジジン)ジメタン	488	10	80	483	>180	>7
19	"	"	"	4,4'-二(2,2,6,6-テトラメチル-5-ヒドロキシ-1,4-ベンジジン)ジメタン	488	25	85	483	>180	>7
20	"	"	"	3,3',5,5'-四(4-tert-butylphenyl)-4,4'-二(2,2,6,6-テトラメチル-5-ヒドロキシ-1,4-ベンジジン)ジメタン	488	20	90	483	>180	>7
21	"	"	"	7,7'-ビス(2,2,6,6-テトラメチル-5-ヒドロキシ-1,4-ベンジジン)ジメタン	488	25	85	483	>180	>7
22	"	"	例 (C14:3,3',5,5'-t)	3,3',5,5'-四(4-tert-butylphenyl)-4,4'-二(2,2,6,6-テトラメチル-5-ヒドロキシ-1,4-ベンジジン)ジメタン	488	20	90	483	>180	>7
23	"	"	例 (C15:3,3',5,5'-t)	"	488	18	90	483	>180	>7
24	"	"	例 (C16:3,3',5,5'-t)	"	488	20	90	483	>180	>7
25	"	"	化合物 (CS)	"	488	10	90	483	>180	>7
26	"	"	化合物 (1)	"	488	8	90	483	>180	>7
27	"	"	化合物 (U)	"	488	8	90	483	>180	>7
28	"	"	例 (D-700):3,3',5,5'-t)	3,3',5,5'-四(4-tert-butylphenyl)-4,4'-二(2,2,6,6-テトラメチル-5-ヒドロキシ-1,4-ベンジジン)ジメタン	488	50	90	483	>180	>7
29	"	"	例 (C40)	"	488	50	80	483	>180	>7
30	"	"	例 (A-771540)	3,3',5,5'-四(4-tert-butylphenyl)-4,4'-二(2,2,6,6-テトラメチル-5-ヒドロキシ-1,4-ベンジジン)ジメタン	488	15	90	483	>180	>7
31	"	"	化合物 (V)	3,3',5,5'-四(4-tert-butylphenyl)-4,4'-二(2,2,6,6-テトラメチル-5-ヒドロキシ-1,4-ベンジジン)ジメタン	488	45	90	483	>180	>7

[0079]The preservability 1 shows the endurance under 25 ** and 60%RH preservation. The preservability 2 shows the endurance under 90 ** preservation.

[0080]

[Effect of the invention] It depends on this invention, it crosses to a large wavelength area, and it becomes it is chemically stable at high sensitivity, and possible to manufacture the volume phase type hologram which has high resolution, high diffraction efficiency, and high transparency simple.

[0081]

[Translation done.]